Acta Chemica Scandinavica, 1997: 51: 274–278
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

An Optically Active Nickel(II) Schiff Base Coordination Compound *N,N'*-(1*R*,2*R*)-(−)-1,2-Cyclohexylenebis(salicylideneiminato)nickel(II)

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Wojtczak, A., Szlyk, E., Larsen, E. and Jaskólski, M., 1997. An Optically Active Nickel(II) Schiff Base Coordination Compound *N,N'*-(1*R*,2*R*)-(−)-1,2-Cyclohexylenebis(salicylideneiminato)nickel(II). – Acta Chem. Scand. 51: 274–278. © Acta Chemica Scandinavica 1997.

The Schiff base between *trans*-(1*R*,2*R*)-1,2-cyclohexanediamine, [$(-)_D$-chxn] and 2 mol of salicylaldehyde has been used as a ligand for nickel(II). The coordination compound has been studied by UV/VIS absorption and circular dichroism spectroscopy in solution, and the crystal structure has been resolved by X-ray diffraction methods. The spectroscopic properties are related to the molecular structure found in the crystal. The crystal system is monoclinic, the unit cell dimensions are $a=10.964(2)$, $b=12.735(3)$, $c=12.329(2)$ Å, $\beta=95.26(3)°$, the volume is 1714.2(6) Å^3 and space group is $P2_1$ with $Z=4$. The final residual is 3.6% for 2785 observed reflections. Two symmetry-independent molecules in the crystal lattice are related by a non-crystallographic two-fold axis. They are involved in an extensive network of stacking interactions. The Ni–Ni distance is 3.403 Å. The two N and O atoms of the tetradentate ligand chelating each central Ni^{II} ion form slightly distorted square-planar environments, the Ni–N distances ranging from 1.848(4) to 1.866(4) Å, and Ni–O distances from 1.835(3) to 1.852(3) Å. The out of plane distortion gives rise to an overall chiral surrounding of the metal ion. The d-d and charge transfer transitions show circular dichroism, and the latter is shown to be consistent with the observed tetrahedral distortion which originates in the (*R,R*) absolute configuration of the ligand.

Schiff bases have been used as very popular ligands because of high stability of the coordination compounds and good solubility in common solvents. The π-system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well. This has given rise to catalytic abilities of cobalt(II) complexes of Schiff base compounds, and the present study is part of a program aimed on the understanding of the molecular properties of such coordination compounds. In this study we employ the rigidity of the cyclohexanediamine derivative of salicylaldehyde, which results in a nearly planar nickel(II) complex with an electronic structure discussed from the absorption and CD spectra.

The study of complexes with optically active ligands is of great interest. Studies of Ni^{II} and Cu^{II} complexes with optically active and sterically demanding tetradentate Schiff bases, among them (−)-chxnsalH_2, were carried out by Downing and Urbach.[1] Authors presented CD and UV/VIS data of the complexes, but the analysis was not supported by the crystal data and band assignment was based on the assumed similarity to the known square planar Ni^{II} complex with the ligand possessing similar chromophoric groups. CD spectra of the Co^{II} complex with the discussed Schiff base were examined by Busetto *et al.*[2] The crystal structure of the *meso* form of [Co(chxn(sal)$_2$)] was reported,[3] in which the tetrahedral distortion from planarity in relation to steric demands of a bulky group in the ethylene bridge has been discussed. Studies of the Co^{II} Schiff base complexes were mostly focused on the explanation of the oxygen binding and catalytic activity of the oxygenated forms.[4–6]

The metal complexes of Schiff base compounds synthesised from the diamines by condensation with acetylacetone (or 2,4-pentanedione) have been investigated by many techniques.[7–10] The structure of [Cu(R-pn(acac)$_2$)] in solution has been studied by absorption and circular

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dichroism spectroscopy, and its crystal structure has been determined by X-ray diffraction methods {[Cu(R-pn-(acacH)$_2$)] is (2*R*)-1,2-propenebis(2,4-pentaneiminato)-copper(II)}.[11,12] The structure of the corresponding nickel(II) compound in solution was discussed on the basis of ^{1}H NMR.[13] Based on these results one may draw the conclusion that [Cu(*R*-pn(acac)$_2$] is significantly distorted towards a tetrahedral structure so that the methyl groups of the diamine and the pentanedione moiety avoid close contact. However, in [Ni(*R*-pn(acac)$_2$)] the two π-systems are nearly coplanar. In these systems the close contact between the two methyl groups is hindered by an unusual conformation of the puckered chelate ring where the methyl group will occupy an axial position. On this basis the structure of analogous coordination compounds can be understood or predicted.

The structure in solution of Schiff base coordination compounds derived from substituted 1,2-ethane-diamines and salicylaldehyde have not been studied in detail by CD, and it is presently difficult to predict how the ligands orient themselves around a metal ion. The reason is that the electronic structure of a salicylaldimine is less suited for stereochemical studies by means of CD because of low effective symmetry, so that the internal $\pi \rightarrow \pi^*$ transition moments are expected to have directions less close to the N–O direction in the plane of the molecule. The earlier studies on such salicylaldimine nickel(II) compounds have not tried to relate circular dichroism to geometric structure but rather assumed a high degree of planarity characteristic for four coordinate nickel(II).

Experimental

Materials. Salicylaldehyde and Ni(CH$_3$COO)$_2$·4H$_2$O, analytical grade, were purchased from Aldrich, whereas (−)-(1*R*,2*R*)-*trans*-cyclohexanediamine (−)chxn was obtained and used *in situ* from *trans*-(1*R*,2*R*)-cyclohexanediammonium (+)$_D$-tartrate made according to Galsbøl's[14] method.

UV/VIS absorption spectra. UV/VIS absorption spectra were recorded using a Milton Roy Spectronic 1201 spectrophotometer. The concentration of the complex was 6.8×10^{-5} M in acetonitrile. The Schiff base spectrum was measured in ethanol (1.46×10^{-4} M) and acetonitrile (1.25×10^{-5} M)

Chiroptical measurements. CD spectra have been measured with a Jasco 720 spectrophotometer for the same sample solution as in the UV/VIS method.

Synthesis. The studied compound was prepared by adding KOH (0.021 mol) in 20 ml of methanol upon stirring to (−)chxn(+)tart (0.01 mol) followed by salicylaldehyde (0.02 mol) in 20 ml of MeOH. The solution was stirred under reflux for 1.5 h. After cooling, a white precipitate was separated from the yellow solution. Ni(CH$_3$COO)$_2$·4H$_2$O (0.01 mol) in 30 ml of methanol was added portionwise to the reaction mixture, followed by KOH (0.02 mol) in methanol. After cooling, a red precipitate was filtered and purified by Soxhlet extraction with ethanol. Red cubic crystals suitable for X-ray analysis were obtained on recrystallization from ethanol solution.

Crystal structure determination

Crystal data and parameters of the data collection are listed in Table 1. Intensities were measured at 293 K on a Syntex diffractometer using graphite monochromated Mo*K*α radiation (λ = 0.71073 Å) by a ω/2θ scan with 2θ in the range 1.0–50.0°. A variable scan speed from 2.00 to 29.30° min^{-1} in ω was applied, with the scan range (ω) 2.04° plus *K*α separation. Two standard reflections were measured every 98 reflections. 3233 reflections were collected ($0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 15$, $-14 \leqslant l \leqslant 14$), of which 3112 were unique, $R_{int} = 1.59\%$. Based on the systematic absences and the data statistics, the space group has been determined as $P2_1$. The structure was solved by direct methods with Siemens SHELXTL PLUS software (PC Version).[15] The full-matrix least-squares refinement against 2785 observed reflections $F > 2.0\sigma(F)$ with statistical weights applied resulted in $R = 3.51\%$, $wR = 3.57\%$, and $S = 3.24$. All non-hydrogen atoms were refined anisotropically, while hydrogens were built from geometry, and the riding model with fixed isotropic thermal parameters was applied. The largest and mean shifts Δ/σ in

Table 1. Crystal data and a summary of data reduction on structure refinement.

Crystal formula	$C_{20}H_{20}N_2NiO_2$
Colour; habit	Dark red parallelepiped
Crystal dimensions	$0.5 \times 0.4 \times 0.5$ mm^3
Crystal system	Monoclinic
Space group	$P2_1$
Unit-cell dimensions at ambient temperature	$a = 10.964(2)$ Å $b = 12.735(3)$ Å $c = 12.329(2)$ Å $\beta = 95.26(3)°$
Volume	$V = 1714.2(6)$ Å^3
Z	4
Relative formula mass	379.1
Density (calc.)	1.469 g cm^{-3}
Absorption coefficient	$\mu = 1.150$ mm^{-1}
$F(000)$	792
Reflections collected	3233
Independent reflections	3112 $R_{int} = 1.59\%$
Observed reflections	2785 $F > 2.0\ \sigma(F)$
Quantity minimized	$w(F_o - F_c)^2$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = s^2(F)$
No. of parameters refined	450
Final *R*-indices (obs. data)	$R = 3.51\%$, $wR = 3.57\%$
R-Indices (all data)	$R = 4.53\%$, $wR = 4.04\%$
Goodness-of-fit	3.24
Largest and mean shifts	0.067, 0.005
Data-to-parameter ratio	6.2:1
Largest difference peak	0.35 e Å^{-3}
Largest difference hole	−0.40 e Å^{-3}

the final refinement cycle were 0.067σ and 0.005σ, respectively. The minimum and maximum peaks in the final difference electron density maps were 0.35 and -0.40 e Å^{-3}. No correction for absorption or extinction was applied. The final positional parameters are given in Table 2, whereas selected bond lengths and bond angles are listed in Table 3.

Table 2. Atomic coordinates and equivalent isotropic displacement coefficients.

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	U(eq)[a]/10^3 Å^2
Molecule I				
Ni	4886(1)	2754	2670(1)	40(1)
O(1)	4939(3)	2435(3)	4125(3)	47(1)
C(1)	4039(5)	2084(4)	4668(4)	45(2)
C(2)	4282(5)	1856(5)	5784(4)	56(2)
C(3)	3385(6)	1511(5)	6397(5)	66(2)
C(4)	2211(6)	1354(6)	5927(5)	76(3)
C(5)	1926(6)	1558(5)	4851(5)	71(3)
C(6)	2835(4)	1928(4)	4192(4)	48(2)
C(7)	2482(5)	2202(4)	3081(4)	48(2)
N(1)	3205(3)	2553(3)	2396(3)	44(1)
C(8)	2710(4)	2883(5)	1290(3)	45(2)
C(9)	1508(4)	2420(5)	828(4)	56(2)
C(10)	1217(4)	2809(6)	−332(4)	66(2)
C(11)	2240(4)	2542(5)	−1059(4)	57(2)
C(12)	3441(4)	3000(5)	−581(4)	49(2)
C(13)	3733(4)	2619(4)	574(4)	44(2)
N(2)	4869(3)	3015(3)	1191(3)	39(1)
C(14)	5737(4)	3473(4)	706(4)	46(2)
C(15)	6885(4)	3789(4)	1226(4)	43(2)
C(16)	7687(5)	4322(5)	611(4)	58(2)
C(17)	8862(5)	4590(5)	1033(4)	58(2)
C(18)	9236(5)	4305(5)	2095(4)	59(2)
C(19)	8467(4)	3777(5)	2730(4)	55(2)
C(20)	7244(4)	3519(4)	2324(4)	43(2)
O(2)	6536(3)	3051(3)	2974(3)	51(1)
Molecule II				
Ni	5167(1)	131(1)	2228(1)	42(1)
O(1)	5118(3)	449(3)	760(3)	45(1)
C(1)	6016(5)	740(4)	202(4)	50(2)
C(2)	5792(5)	861(5)	−926(4)	57(2)
C(3)	6690(6)	1185(6)	−1539(5)	78(3)
C(4)	7896(6)	1391(6)	−1080(5)	83(3)
C(5)	8108(6)	1288(5)	41(5)	71(3)
C(6)	7220(5)	960(4)	696(4)	50(2)
C(7)	7502(5)	918(4)	1843(4)	50(2)
N(1)	6781(3)	581(3)	2535(3)	42(1)
C(8)	7097(4)	648(4)	3719(4)	48(2)
C(9)	8461(4)	731(5)	4103(4)	63(2)
C(10)	8609(5)	735(5)	5361(5)	74(3)
C(11)	7993(5)	−176(5)	5851(4)	62(2)
C(12)	6620(4)	−236(5)	5444(4)	50(2)
C(13)	6514(4)	−291(4)	4196(4)	46(2)
N(2)	5246(3)	−324(3)	3656(3)	43(1)
C(14)	4378(4)	−688(5)	4156(4)	50(2)
C(15)	3120(4)	−829(4)	3684(4)	46(2)
C(16)	2272(5)	−1260(5)	4341(4)	58(2)
C(17)	1072(5)	−1377(5)	3949(5)	65(2)
C(18)	713(5)	−1107(5)	2874(4)	61(2)
C(19)	1531(5)	−702(5)	2216(4)	63(2)
C(20)	2772(5)	−557(5)	2585(4)	48(2)
O(2)	3526(3)	−189(3)	1921(3)	56(1)

[a]Equivalent isotropic U, defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond distances d and bond angles α.

	d/Å	
Bond	Molecule I	Molecule II
Ni–O(1)	1.835(3)	1.850(3)
Ni–O(2)	1.852(3)	1.850(3)
Ni–N(1)	1.861(4)	1.848(4)
Ni–N(2)	1.852(4)	1.866(4)
O(1)–C(1)	1.320(6)	1.303(6)
C(6)–C(7)	1.432(7)	1.458(7)
N(1)–C(8)	1.483(6)	1.486(6)
C(8)–C(13)	1.527(7)	1.502(8)
C(13)–N(2)	1.467(6)	1.471(6)
C(14)–C(15)	1.418(7)	1.421(7)
C(15)–C(20)	1.418(7)	1.430(7)
C(1)–C(6)	1.408(7)	1.417(7)
C(7)–N(1)	1.290(7)	1.268(7)
C(8)–C(9)	1.507(7)	1.535(7)
C(12)–C(13)	1.511(7)	1.530(7)
N(2)–C(14)	1.306(6)	1.288(7)
C(15)–C(16)	1.390(8)	1.365(9)
C(20)–O(2)	1.309(6)	1.305(6)
	α/1°	
Bond angle	Molecule I	Molecule II
O(1)–Ni–N(1)	95.1(2)	94.9(2)
O(1)–Ni–N(2)	177.3(2)	174.8(2)
N(1)–Ni–N(2)	85.7(2)	86.7(2)
O(1)–Ni–O(2)	84.5(1)	84.7(1)
N(1)–Ni–O(2)	175.9(2)	174.3(2)
N(2)–Ni–O(2)	94.8(2)	94.2(2)
Ni–O(1)–C(1)	127.8(3)	127.8(3)
O(1)–C(1)–C(6)	123.5(4)	123.9(4)
C(2)–C(1)–C(6)	117.7(5)	116.5(5)
C(1)–C(6)–C(7)	121.7(5)	120.9(5)
C(6)–C(7)–N(1)	125.5(5)	125.1(5)
Ni–N(1)–C(7)	126.0(3)	127.3(3)
Ni–N(1)–C(8)	113.7(3)	112.2(3)
C(7)–N(1)–C(8)	120.3(4)	120.3(4)
N(1)–C(8)–C(9)	118.1(4)	115.6(4)
N(1)–C(8)–C(13)	104.0(4)	105.1(4)
C(8)–C(13)–C(12)	111.8(4)	111.9(4)
C(8)–C(13)–N(2)	104.8(4)	105.8(4)
C(12)–C(13)–N(2)	117.9(4)	116.5(4)
Ni–N(2)–C(13)	112.0(3)	110.6(3)
Ni–N(2)–C(14)	126.1(3)	126.6(3)
C(13)–N(2)–C(14)	121.9(4)	122.3(4)
N(2)–C(14)–C(15)	125.0(4)	125.5(5)
C(14)–C(15)–C(16)	118.2(4)	119.4(5)
C(14)–C(15)–C(20)	121.4(5)	121.6(5)
C(16)–C(15)–C(20)	120.4(4)	118.8(5)
C(15)–C(20)–O(2)	124.6(4)	122.9(5)
Ni–O(2)–C(20)	126.3(3)	128.5(3)

Results and discussion

Spectroscopic measurements. Free ligand absorption and circular dichroism spectra in ethanol reveal a long-wavelength CD at 325 nm (Table 4). This CD band and the associated absorption is assigned as essentially due to $n\rightarrow\pi^*$ transitions, whereas the Cotton effects with a minimum CD at 264 nm and a maximum CD at 242 nm are the results of exciton-coupled $\pi\rightarrow\pi^*$ transitions in

Table 4. CD, UV–VIS spectral data for [Ni((−)chxn(sal)$_2$)] and (−)$_D$-chxn(salH)$_2$.

CD	Absorption	
λ/nm (Δε/cm^{-1} M^{-1})	λ/nm (ε/cm^{-1} M^{-1})	Type
(−)-chxn(salH)$_2$		
325 (−10)	405 (600)	n→π*
263 (−39)	315 (3100)	π→π*
242 (+52)	254 (8500)	π→π*
Ni((−)chxn(sal)$_2$)		
570 (+0.1)	552 (34)	d→d
506 (−0.05)		d→d
466 (+0.8)		d→d
437 (+0.5)		d→d
407 (−1.5)	407 (4570)	LMCT
368 (+0.5)		LMCT
337 (−1.0)	337 (5260)	LMCT
258 (−5.5)		LMCT

the molecule considered as two weakly interacting chromophores. The splitting between the bands is much larger than the energy splitting because of near cancellation of two large CD bands of opposite sign giving rise to the observed residuals. The wing shape for the CD components is typical for exciton-coupled transitions. For the ligand derived from cyclohexanediamine and salicylaldehyde the two exciton components can be predicted to have CD spectra in close analogy to those of (−)-chxn(acacH)$_2$, because for both molecules the electronic transition moment in each planar π system has a direction in the plane and relatively close to the line between N and O.[7] The two CD components of the π→π* transitions in (−)-chxn(salH)$_2$ have approximately the same rotational strengths and can therefore be considered to represent a relatively pure exciton couplet.

The absorption spectrum of [Ni((−)chxn(sal)$_2$)] shows a weak absorption in the 500 nm range with CD components at 570 nm (0.12), 506 nm (−0.046) and 466 nm (0.80) (Table 4). These CD bands are interpreted as transitions from the weakly σ-antibonding 3d orbital, the π-antibonding and, the non-bonding orbitals, respectively, to the strongly σ-antibonding 3d orbital. The latter transition, which can be described as a $xy \rightarrow x^2-y^2$ transition, has a large rotatory strength as expected for a transition with a large magnetic transition moment. The higher energy bands at 437, 407, 368 and 337 nm are all considered to be charge transfer bands, where electronic transitions may take place from internal ligand π orbitals and non-bonding oxygen orbitals to the strongly antibonding 3d orbital (x^2-y^2, when O,N,N,O are placed at the x- and y-axes). The dominating sign for these CD bands is negative. They are very different in this respect from exciton-coupled transitions which integrate to zero. The π→ d transitions obtain an electric transition moment, P, which is defined from the atomic arrangement in the mean coordination plane. The magnetic transition moment, M, associated with the same transition is mainly derived from the tetrahedral out-of-plane distortion as a charge rotation during the transition. To produce a negative rotational strength $R=PM$ the distortion has to take the shape shown in Fig. 1, and not its mirror image. Because of the low effective symmetry in this coordination compound only detailed calculations can explain the two small positive CD bands and the numerical details

Description of the crystal structure. There are two molecules in the asymmetric unit, and this is consistent with the $P2_1$ space group, cell volume, density and molecular formula. The two independent molecules in the asymmetric unit have nearly identical structure (Fig. 2). In both symmetry-independent molecules four atoms of the ligand chelating the central Ni^{II} ion form the slightly distorted square-planar environment. The observed bond lengths and bond angles conform with those values measured for similar coordination compounds.[16–19] For instance, the Ni–O and Ni–N bond distances are in good agreement with those reported for [Ni(salen)],[16] while Ni–N are only slightly longer than those observed in [Ni(naphten)]. The two independent molecules have small differences, just as there are differences between the two halves of each molecule. These differences are considered to arise from packing effects.

The nearly planar coordination spheres of each Ni^{II} are slightly tetrahedrally distorted. In both molecules the deviations from the best plane Ni–O–N–N–O are small,

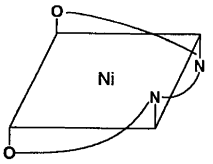

Fig. 1. Distortions from the average coordination plane in [Ni((−)chxn(sal)$_2$)].

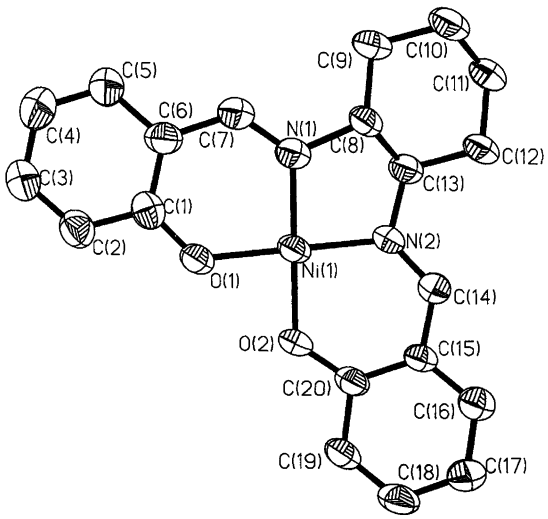

Fig. 2. ORTEP drawing of the molecule I of [Ni((−)chxn(sal)$_2$)] with the non-hydrogen atoms labelled. The thermal ellipsoids are plotted with 40% probability.

Table 5. The deviations of selected atoms from the Ni–O–N–N–O best planes calculated for the two molecules.

Atom	Distance/Å	
	Molecule I	Molecule II
Ni	−0.0096	−0.0042
O1	−0.0522	−0.0862
N1	0.0560	0.0864
N2	−0.0512	−0.0844
O2	0.0570	0.0884

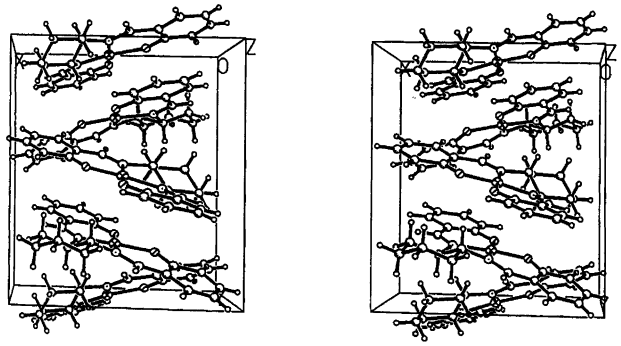

Fig. 3. Packing diagram of [Ni((−)chxn(sal)$_2$)], projected along the crystallographic *z*-axis. The pair of molecules in the asymmetric unit is related by a non-crystallographic twofold axis of symmetry.

but statistically significant and of the same chirality. The deviations are listed in Table 5. These small distorsions are the reason for the observed negative CD in the charge-transfer region mentioned above. The distortions are slightly more pronounced in molecule II than in molecule I, but are much smaller than those found in [Co(meso-chxn(sal)$_2$)][3] and as one might infer from strain considerations greater than reported for [Ni(salen)].[16] The distortions may be explained by intermolecular steric effects on the ligand atoms in the coordination plane. In fact one may reverse the issue and explain the near-planarity by a nearly complete cancellation of atomic charges in the inner complex.

The absolute configuration of the ligand's chiral centres was known from the synthesis. It was further checked to be in agreement with this data according to the Rogers method.[20] The reported enantiomorph gave $R=0.0351$, while the mirror image gave $R=0.0371$. The cyclohexane rings are found in the chair conformation. In this ring alternate torsion angle values for the subsequent C–C bonds are close to 56 and −56° in both molecules.

The packing diagram (Fig. 3) revealed the stacking interactions between pairs of complex molecules related by a non-crystallographic two fold axis. This introduces a series of intermolecular contacts of 3.2–3.9 Å. The contacts involve the phenyl ring carbon atoms of adjacent molecules, as well as the central ions and ligating atoms. The intermolecular distances between nickel from one coordination entity and oxygen from the other are 3.786 and 3.775 Å, respectively, while the corresponding nickel nitrogen distances are 3.473 and 3.777 Å, respectively. The distance between the two independent nickel ions in the unit cell is 3.403 Å, and with these distances the interactions are considered solely to be made up of intermolecular forces.

Acknowledgements. This work was supported by the PECO EEC program and the COST D1 Chemistry initiative. E. L. gratefully acknowledges support from the Danish Natural Research Council.

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Received April 24, 1996.